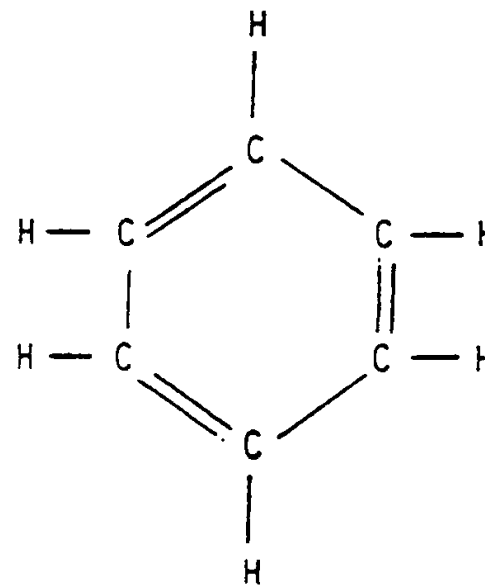


Chemistry I



Chemical Bonding

Chemical Bonding

1. Bonding in any element will take place with only the *valence shell electrons*.
2. The valence shell electrons are found in the outermost energy level.
3. By looking at the electron configuration and the Periodic Table one is able to identify the valence electrons.

Why chemical bonding occurs

- ▶ Chemical bonding occurs:
 - So atoms can achieve maximum stability
 - By reducing potential energy
 - By reaching Noble gas configuration
- ▶ All bonding forces are due to electrostatic charge.
 - Opposite charges attract, Like charges repel.

The Octet Rule

- ▶ The octet rule says that atoms tend to gain, lose or share electrons so as to have eight electrons in their outer electron shell.
- ▶ But there are *many* bonding situations where it does *not* apply.

Exceptions to the Octet Rule (Lewis structures)

1. Elements in the third period and below can accommodate more than an octet of electrons. elements such as Si, P, S, Cl, Br, and I, under some circumstances form more bonds than the rule allows.
2. Some stable molecules simply do not have enough electrons. This usually occurs in compounds containing Be or B.
3. Free Radicals

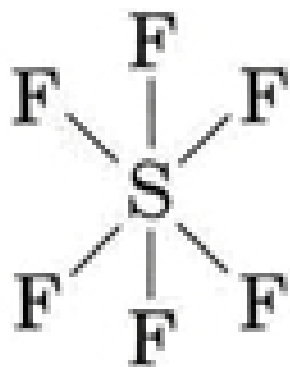
Exceptions to the Octet Rule

Expansion

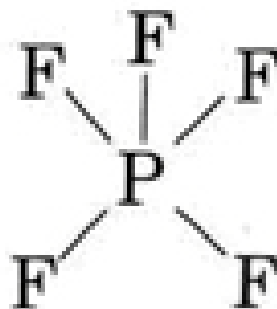
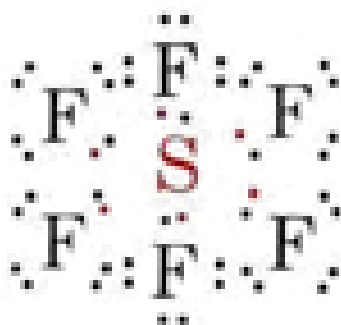
Atoms, which have room for more than 8 electrons in their outer shell, may form bonds, which result in 10, 12, or 14 outer shell electrons being shared.
(even numbers are stable)

Exceptions to the Octet Rule Expansion

Examples:



or

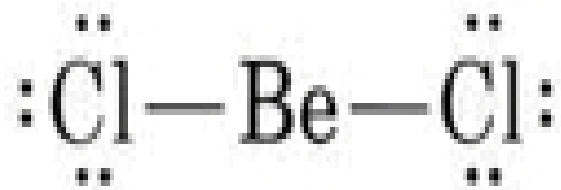


or



Exceptions to the Octet Rule when there are not enough

examples of this exception are provided by
 BeCl_2 and BCl_3 .

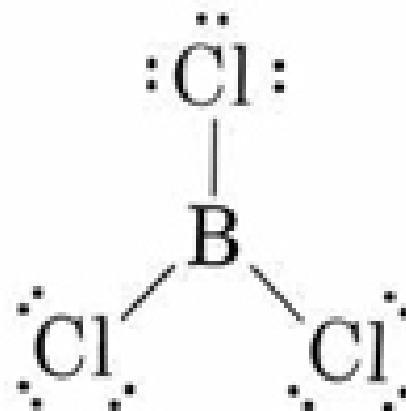


Since Cl atoms do not readily form multiple bonds, we expect the Be atom to be joined to each Cl atom by a single bond.

Instead of an octet the valence shell of Be contains only *two* electron pairs.

Exceptions to the Octet Rule when there are not enough

Similar arguments can be applied to boron trichloride, BCl_3 , which looks like this:



The valence shell of boron has only three pairs of electrons

Exceptions to the Octet Rule when there are not enough

Molecules such as BeCl_2 and BCl_3 are referred to as **electron deficient** because some atoms do not have complete octets.

Exceptions to the Octet Rule

Free Radicals

There are a few stable molecules which contain an odd number of electrons.

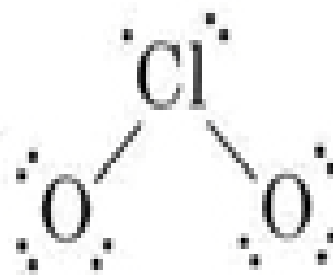
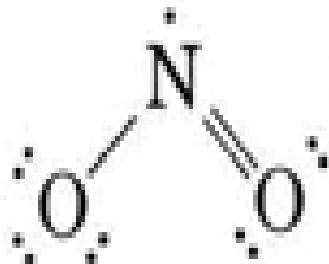
These molecules, called "*free radicals*", contain at least one unpaired electron, a clear violation of the octet rule.

Free radicals play many important roles a wide range of chemistry fields.

Exceptions to the Octet Rule

Free Radicals

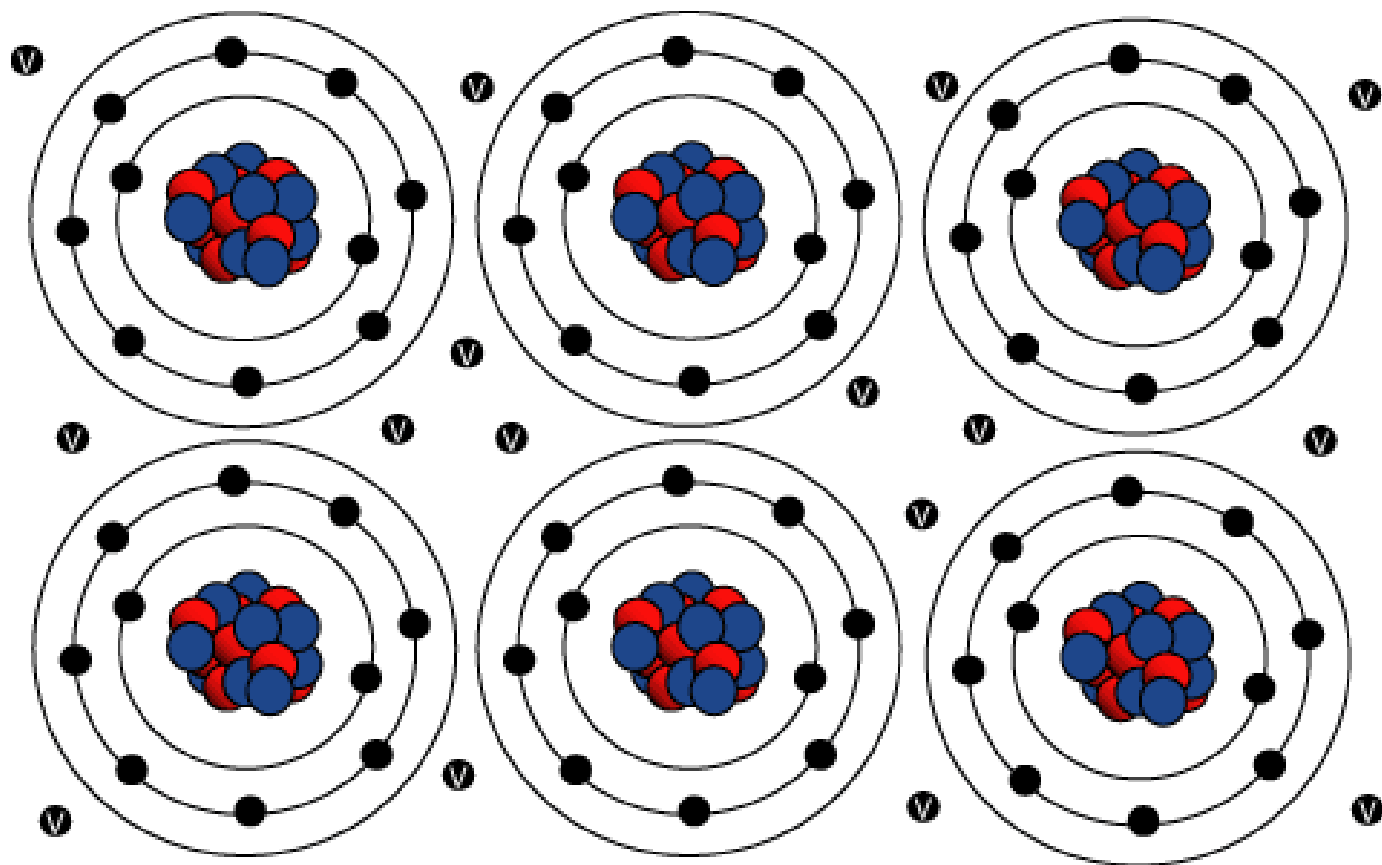
Three well-known examples of such molecules are nitrogen (II) oxide, nitrogen(IV) oxide, and chlorine dioxide. *The most plausible Lewis structures for these molecules are:*



Metallic bonding

1. Occurs between atoms of the same metal
2. Atoms have 1,2 or 3 valence electrons, therefore there are many *vacancies in valence shell*.
3. Nuclei of the atoms are in a sea of electrons
4. When electron clouds overlap, *electrons can move into electron cloud of adjoining atoms*

Metallic bonding



Properties of substances with metallic bonding

- 1) Metals are dense because the atoms in metals are tightly packed in the lattice.
- 2) Metals have high melting and boiling points because strong forces of attraction exist between particles and these forces operate throughout the crystal.

Properties of substances with metallic bonding

3) Metals are good conductors of heat because delocalized electrons transmit the energy to its neighbors.

4) Metals are good conductors of electricity because electrons can flow within the lattice or crystal

Properties of substances with metallic bonding

5) Metals are malleable and ductile because bending and stretching does not disrupt the metallic bonds.

6) Metals are lustrous (shiny) because presence of free electrons causes most metals to reflect light.

Ionic Bonding

occurs between *metals* and *non-metals*..

- **Metal** atoms have a *low number of valence electrons* and a *low electronegativity*.
- **Non-metal** atoms have *numerous valence electrons*.

Ionic Bonding

If the electron clouds overlap (bond)..

Metals

- lose valence electrons
achieve a stable valence shell (usually 8 e⁻)
gains a positive charge, i.e. a positive ion.

Non-metals

- gain valence electrons
achieve a stable valence shell (usually 8 e⁻)
- Will gain a negative charge i.e.. a negative ion

Formation of positive ions (cations)

The charge is the number of valence e^{-1} 's it has to lose.

- 1) Na atom $[\text{Ne}] 3s^1$ loses one electron to become a sodium ion (Na^{+1}) with $[\text{He}] 2s^2 2p^6$ configuration
- 2) K atom $[\text{Ar}] 4s^1$ loses one electron to become a potassium ion (K^{+1}) with $[\text{Ne}] 3s^2 3p^6$ configuration.

This is common for ALL Group 1 elements.

Formation of positive ions (cations)

3) Mg atom $[\text{Ne}]3s^2$ loses 2 electrons to become a magnesium ion (Mg^{+2}) with $[\text{He}] 2s^2 2p^6$ configuration

4) Ca atom $[\text{Ar}] 4s^2$ loses 2 electrons to become a calcium ion (Ca^{+2}) with $[\text{Ne}] 3s^2 3p^6$ configuration.

This is common for ALL Group 2 elements.

Formation of positive ions (cations)

5)Al atom [Ne] $3s^23p^1$ loses 3 electrons to become an aluminum ion (Al^{+3}) with [He] $2s^22p^6$ configuration.

This is common for **Group 13 metals ONLY**

General note: metals will always make positive ions.

Formation of negative ions (anions)

- 1) F atom $[\text{He}] 2s^2 2p^5$ goes to the fluoride ion (F^{-1}) with $[\text{He}] 2s^2 2p^6$
- 2) Cl atom $[\text{Ne}] 3s^2 3p^5$ goes to the chloride ion (Cl^{-1}) with $[\text{Ne}] 3s^2 3p^6$

Formation of negative ions (anions)

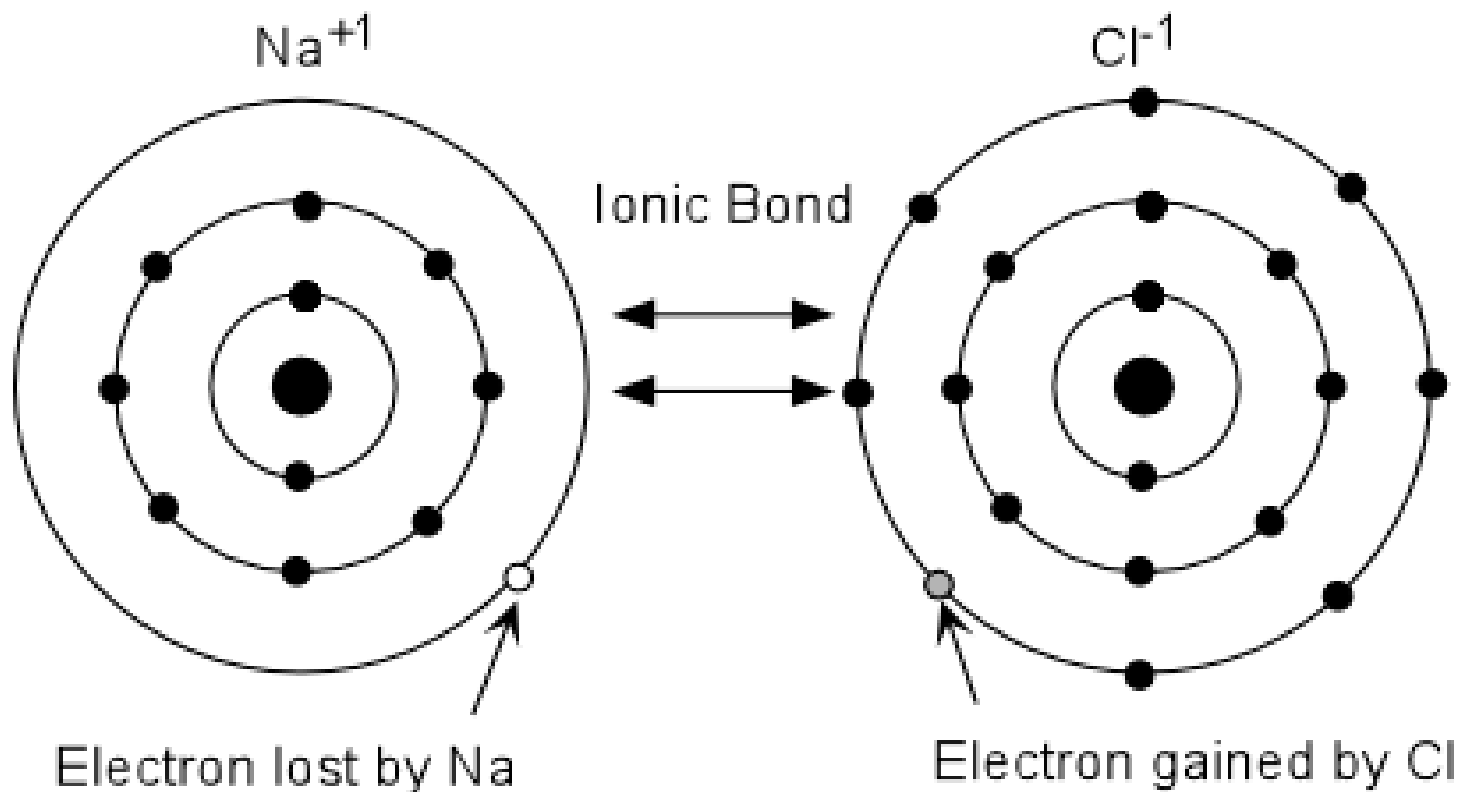
1. O atom $[\text{He}] 2s^2 2p^4$ goes to the oxide ion (O^{2-}) with $[\text{He}] 2s^2 2p^6$
2. The charge is the number of electrons needed to get 8 in the outermost level and make the charge negative.
Ex: O gains 2 e^- and has -2 charge
3. Nonmetals will **usually** make negative ions.

Formation of ionic compounds

The positive and negative ions will attract each other to form a three dimensional continuous lattice structure (or crystal).

- ❖ Each positive ion is surrounded by a number of negative ions.
- ❖ Each negative ion is surrounded by a number of positive ions.
- ❖ The ratio of positive to negative ions in the lattice is determined by the charges of the ions

Formation of ionic compounds



Properties of Ionic compounds and why they have these properties

1) Melting point and boiling point are high because a large amount of thermal energy is required to separate the ions.

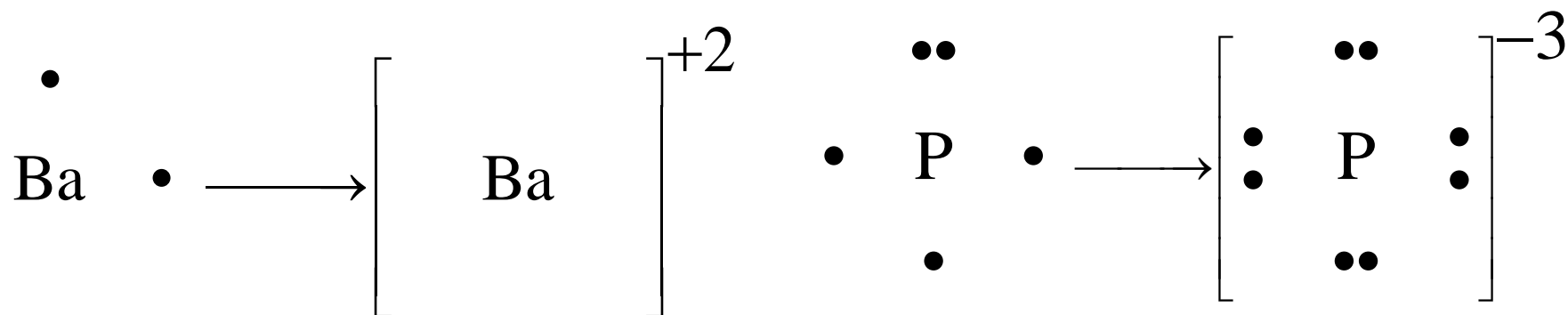
2) Electrical conductivity is poor because there are no free electrons.

Properties of Ionic compounds and why they have these properties

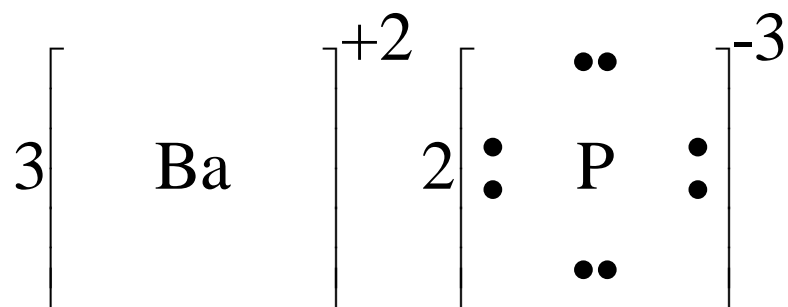
3) The crystals of ionic compounds are hard because the ions are bound strongly to the lattice and aren't easily displaced.

4) The crystals of ionic compounds are brittle because distortion causes ions of like charges to come close together then sharply repel.

Lewis Structures of Ionic compounds



Now to combine the two



Covalent Bonding

Bonding between *non-metals* and *non-metals*.

- Therefore all atoms included have *fairly high electronegativity* and *few vacancies in valence energy levels*.
- When they bond, they gain electrons to achieve stable configuration.
- Hence, **electrons are shared as pairs.**

Covalent Bonding

Sharing produces low energy (stable) electron arrangements that are isoelectronic (same # e^{-1} as) with the Noble gases.

ie:

- Full outer shell (eg He $1s^2$; Ne $1s^2 2s^2 2p^6$)
8 electrons (4 pairs) in outer shell (eg Ar $1s^2 2s^2 2p^6 3s^2 3p^6$)

When more than one pair of electrons are shared

1. There are some situations in covalent bonding where there are insufficient electrons.
2. When this occurs, atoms will share multiple pairs of electrons.
3. Carbon is one of the elements that does this quite readily.

Covalent bonds

When two atoms share 1 pair of electrons, the bond is called a **single covalent bond**.

When two atoms share 2 pairs of electrons, the bond is called a **double covalent bond**.

When two atoms share 3 pairs of electrons, the bond is called a **triple covalent bond**.

Covalent bonding

Covalence is the number of electrons an atom needs to produce a stable outer shell.(how many does it need to get to meet the octet rule.)

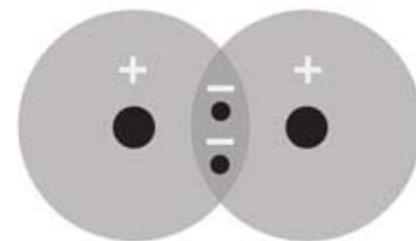
The number of *shared pairs (covalent bonds)* of electrons an atom forms.

eg Hydrogen *H* needs 1 additional electron therefore the covalence is 1

Covalent bonding in the hydrogen molecule

When hydrogen bonds it bonds with 1 pair of e⁻'s shared between 2 atoms – a *covalent bond*.

Shared pair of electrons



Hydrogen Molecule (H₂)



Covalent bonding in the hydrogen molecule

Hydrogen molecule consists of 2 covalently bonded hydrogen atoms, which have no tendency to bond further (both have achieved a stable outer shell).

Each molecule exists independently

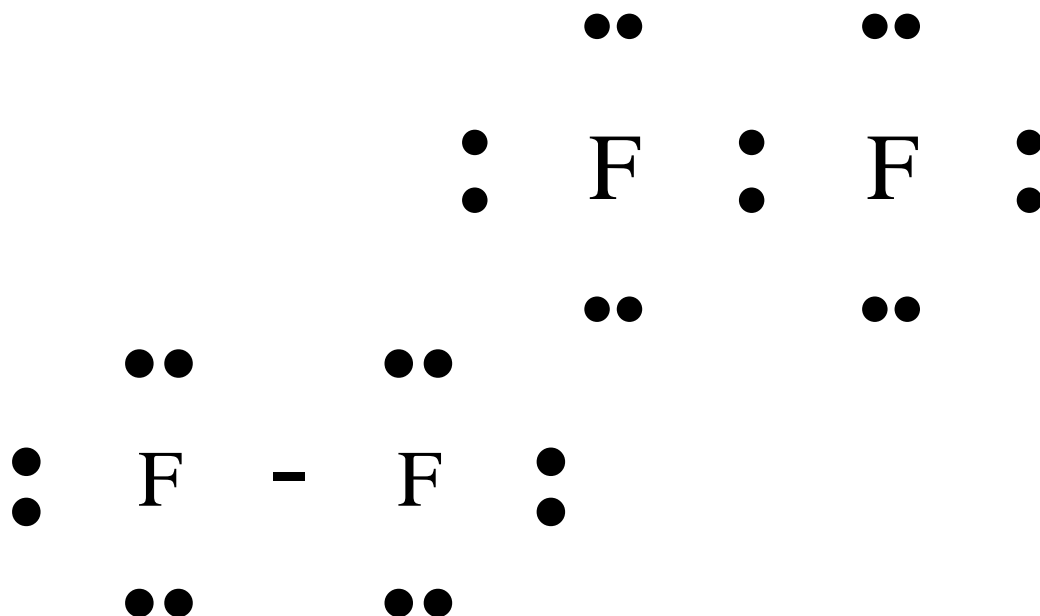
Covalent bonding in the hydrogen molecule

Bonding pairs of electrons orbits both nuclei and are attracted to both nuclei

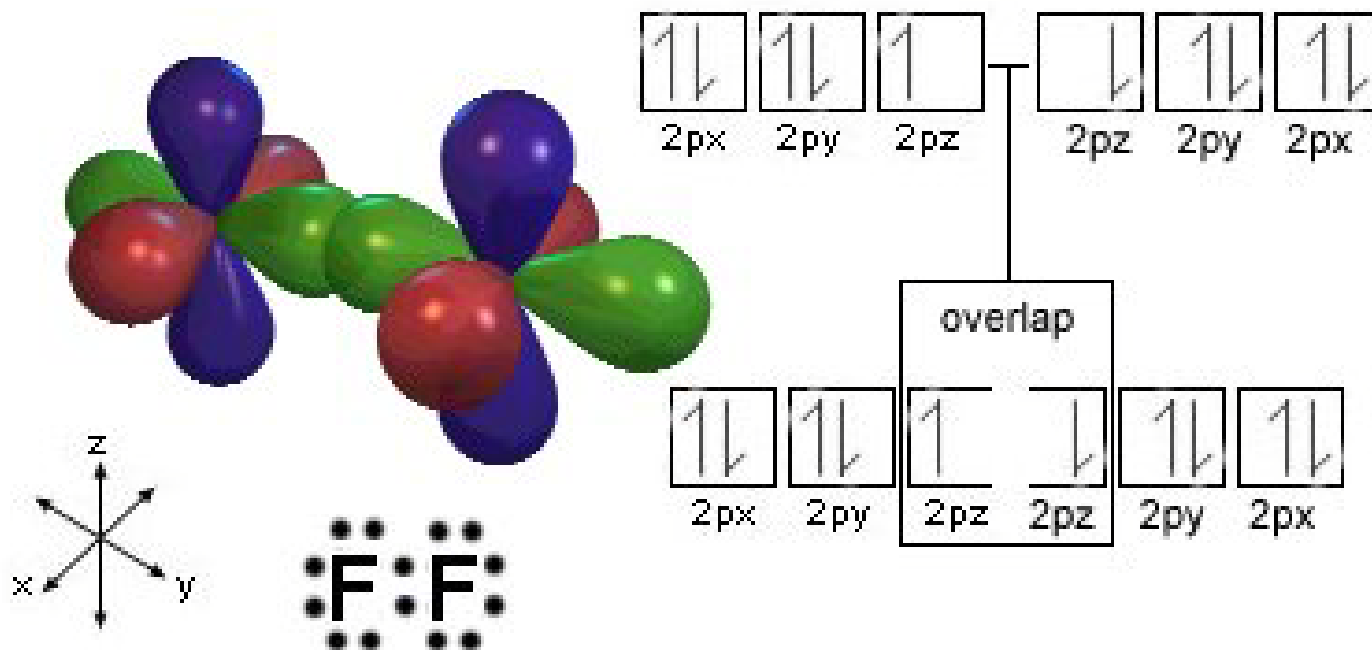
These attractions provide the bonding force.

Covalent bonding in other diatomic molecules

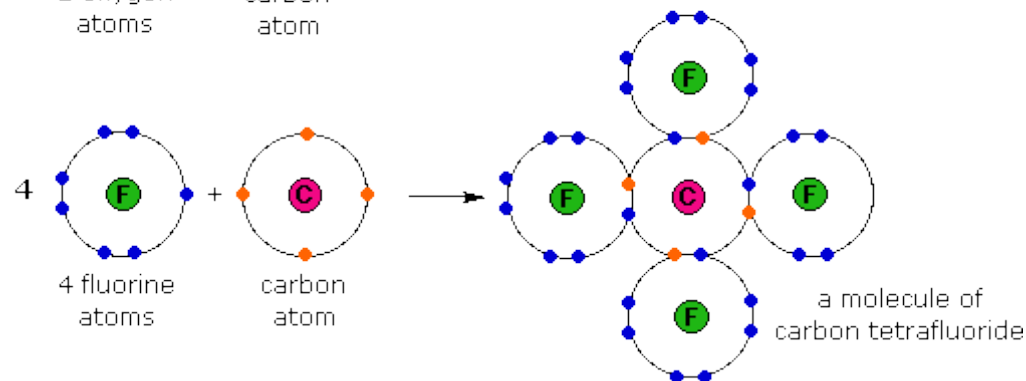
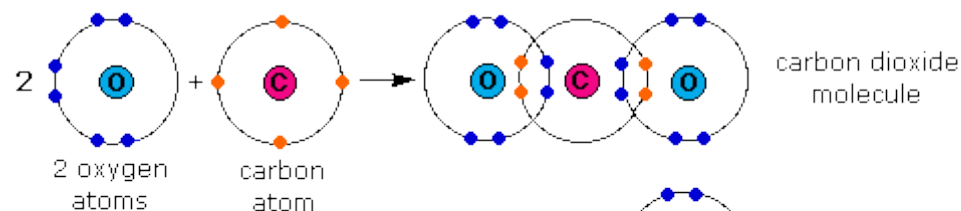
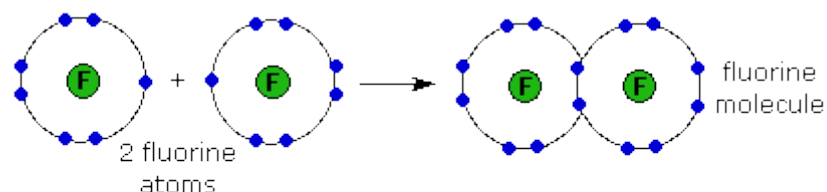
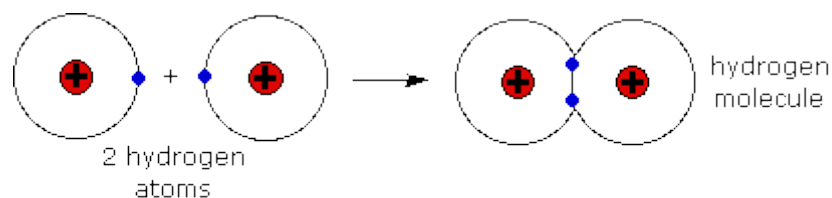
eg Fluorine F [He] $2s^2 2p^5$ needs one electron to achieve Noble gas configuration.



Fluorine covalent bonding



Covalent Bonding Examples



Not ALL electrons are shared equally in a covalent bond

In covalent bonds, where the electronegativities are equal between the two atoms, the atoms share electron pair equally (**pure covalent**).

In covalent bonds, where the electronegativities are not equal, the atom with the higher electronegativity will have a greater pull on the shared electron pair.

Polar covalent bonds

This atom in the bond “hogs” the shared electron pair (usually the most electronegative atom).

The atom tending to “hog” the electron pair acquires a slight *negative charge* ($\delta -$)

The atom tending to “lose” electron pair acquires a slight *positive charge* ($\delta +$)

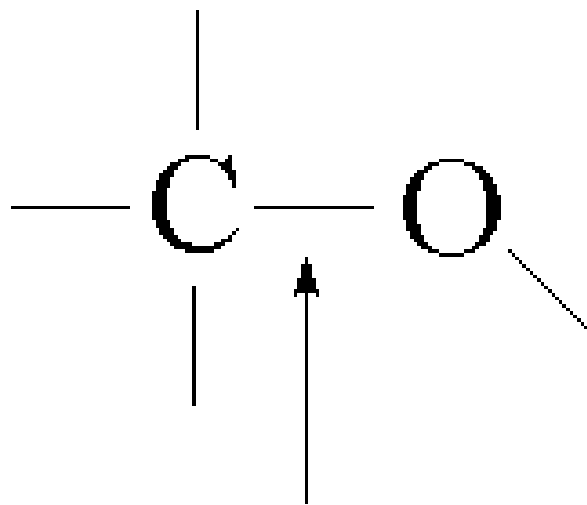
This bond is called a **polar covalent bond**.

Polar covalent bond

The difference between C and O electronegativities is **1.0 Pauling unit**.

(3.5 - 2.5 = 1.0)

Therefore the bond between these 2 atoms is **polar covalent**.



Polar Covalent Bond

Electronegativity

Periodic Table Of Elements

1

1

2

3

4

11

12

19

20

37

38

55

56

87

88

Atomic Number

Element Symbol

Electronegativity Value in Pauling units

38

Sr

1.0

13

14

15

16

17

13

14

15

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17

18

31

32

33

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49

50

51

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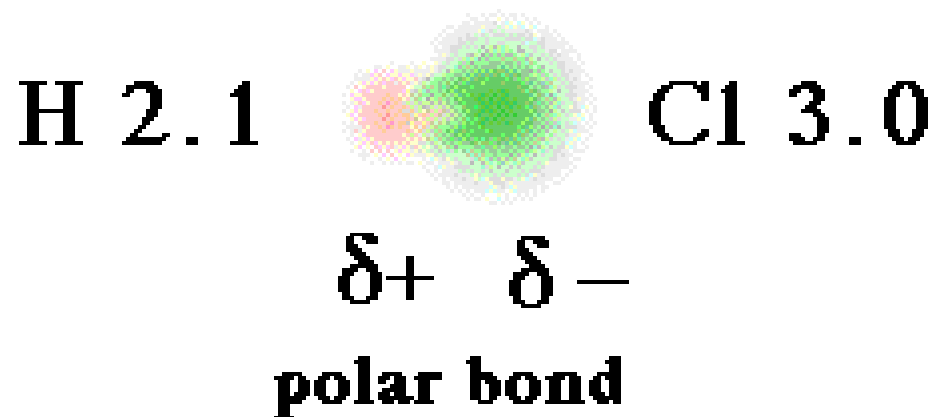
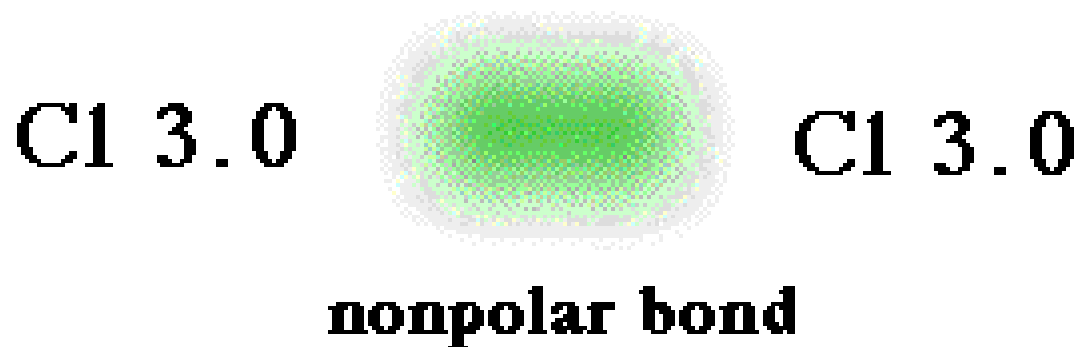
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bond type	electronegativity difference
nonpolar covalent	0.0-0.3
polar covalent	0.4-1.6
ionic	1.7-3.2

Covalent Bonds



Polar covalent bonds

Not to be confused with



Co-ordinate Bonds

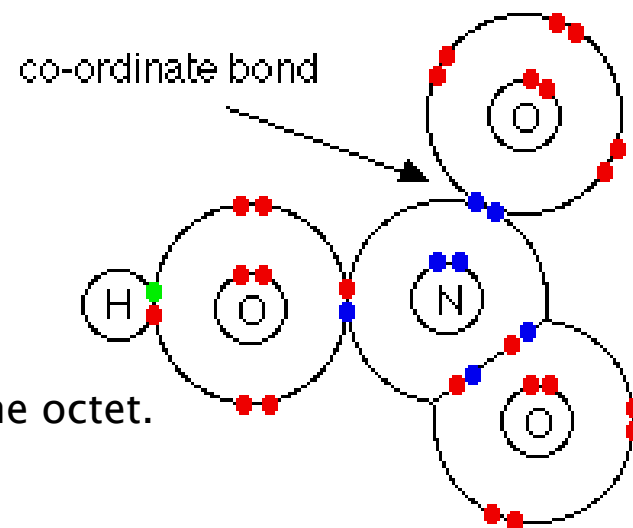
A rare covalent bond that occurs when the **shared pair of e⁻'s** in a covalent bond is **provided by 1 atom**.

It is represented by an arrow, showing the direction in which the shared e⁻'s are provided.

- eg HNO_3

Co-ordinate bonds aren't very common.

They usually occur in atoms that cannot expand the octet.



Properties of covalently bonded compounds

1) Do not conduct electricity because the electrons are tightly bound to atoms or shared by atoms in covalent bonds and do not move.

2) Melting and boiling points are low because Forces of attraction between molecules are weak and little energy is required to separate them.

Properties of covalently bonded compounds

3) Molecules are soft because they are weakly attracted to each other and are easily displaced and there are no bonds between the molecules.

4) Covalent compounds aren't usually very soluble in water because these compounds tend to dissolve in other compounds that have similar properties (particularly polarity).

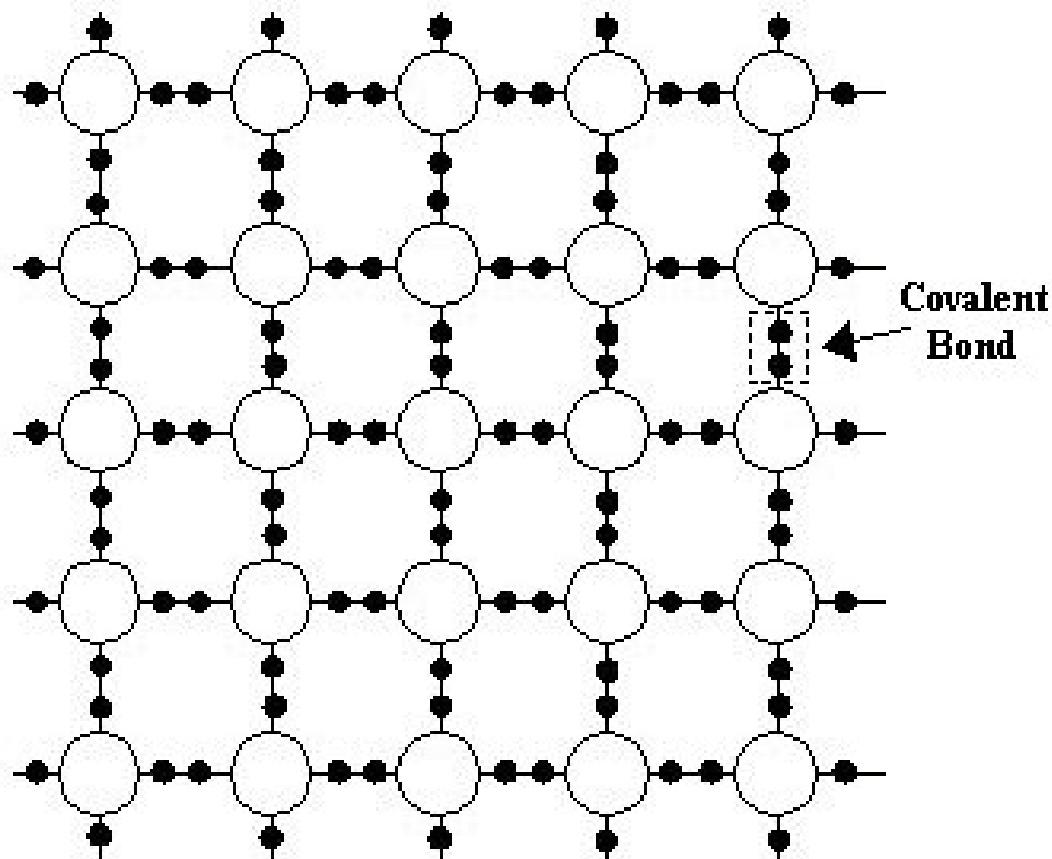
Covalent Network (Lattice)

Bonding between non-metals.

Form covalent bonds between the atoms (shared electron pairs).

Do not form **separate (discrete) molecules** but a *continuous network*.

Examples of covalent crystals



Properties of Covalent Network Compounds

1. Covalent Network Compounds are poor conductors of electricity because electrons are held either on the atoms or within covalent bonds. They cannot move through the lattice.
2. Covalent Network Compounds melting points are very high melting because each atom is bound by strong covalent bonds. Many covalent bonds must be broken if the solid is to be melted and a large amount of thermal energy is required for this.

Properties of Covalent Network Compounds

3. These compounds are hard because the atoms are strongly bound in the lattice, and are not easily displaced.
4. Covalent network substances are brittle. If sufficient force is applied to a crystal, covalent bonds are broken as the lattice is distorted. Shattering occurs rather than deformation of a shape.

Intermolecular Forces

Covalent Compounds

London forces – all molecules have the capability to form London forces.

These are the only types of forces that non-polar covalent molecules can form.

They result from the movement of the electrons in the molecule, which generates temporary positive and negative regions in the molecule.

Intermolecular Forces

Covalent Compounds

Dipole–dipole forces – only polar covalent molecules have the ability to form dipole–dipole attractions between molecules.

Polar covalent molecules act as little magnets; they have positive ends and negative ends that attract each other.

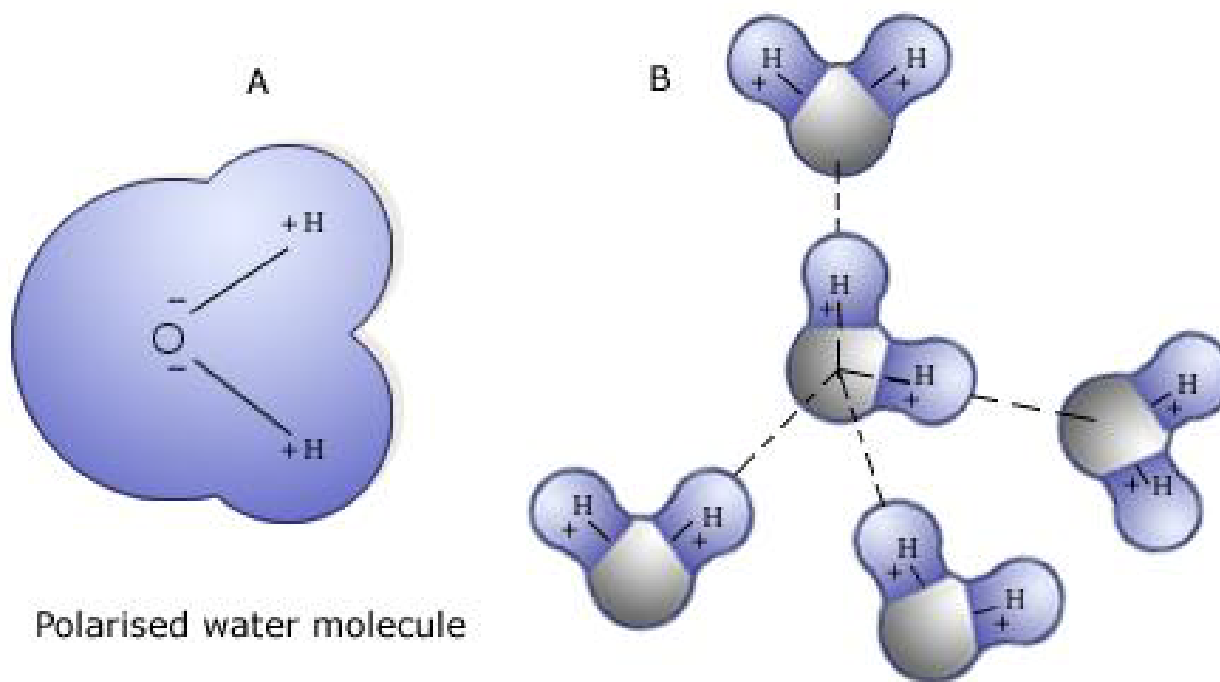
Intermolecular Forces

Covalent Compounds

Hydrogen bonding – these occur between polar covalent molecules that possess a hydrogen bonded to an extremely electronegative element, specifically – N, O, and F.

Water is a major example of this type of bonding and explains why the mp and bp of water are so high.

H-bonding in water



Polarised water molecule

(A) Polarised covalent bonds link the hydrogen and oxygen atoms in a water molecule. (B) Hydrogen bonds between adjacent water molecules. Hydrogen bonds are represented in diagrams by dashed or dotted lines, and covalent bonds by solid lines.

Intermolecular Forces

Ionic Compounds and Metals

Ionic Compounds and Metals

Electrostatic forces – these forces occur between charged species and are responsible for the extremely high melting and boiling points of ionic compounds and metals.

Relative strength of IMF's

IMF	Relative strength	Interacting Particles
London	weak	all types of molecules
Dipole–dipole	mildly strong	polar molecules ONLY
Ion–dipole	medium strong	ions & polar molecules
H–bonding	moderately strong	hydrogen bonded to an extremely electronegative element, specifically – N, O, and F.
Electrostatic	extremely strong	ions and metal atoms

Molecular Geometry

The way that some atoms covalently bond together will cause them to have a particular molecular shape.

There are three theories that attempt to explain this:

- VESPER theory
- Valence Bond Theory
- Molecular orbital theory

VESPER theory

The valence shell electron–pair repulsion model (VSEPR) was devised to account for these molecular shapes.

In this model, atoms and pairs of electrons will be arranged to minimize the repulsion of these atoms and pairs of electrons.

VESPER theory

A simple model for demonstrating the behaviour of electron pairs under the influence of their mutual repulsion is provided by a set of spherical balloons of equal size.

Four balloons tied together so that they squeeze each other fairly tightly, they inevitably adopt the *tetrahedral* arrangement shown for CH₄ in Table 1.

VESPER theory

Although it is possible to flatten the balloons on a table until they are all in the same plane, they invariably spring back to the tetrahedral configuration as soon as the pressure is removed.

A similar behaviour is found if two, three, five, or six balloons are tightly tied together, except that in each case a different stable shape is adopted once the balloons are left to themselves.

Formula	Lewis Structure	Molecular Geometry
HBr	$\text{H}-\ddot{\text{Br}}:$	linear
NH_3	$\begin{array}{c} \text{H}-\ddot{\text{N}}-\text{H} \\ \\ \text{H} \end{array}$	pyramidal
CH_4	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \end{array}$	tetrahedral
H_2O	$\begin{array}{c} \text{H} \\ \\ \text{H}-\ddot{\text{O}}: \end{array}$	bent
C_2H_4	$\begin{array}{ccc} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} & \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$	triangular

Hybridization

The solution to the Schrodinger Equation provides for the following atomic orbitals:

$1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f$, etc.

An atomic orbital is really the energy state of an electron bound to an atomic nucleus. The energy state changes when one atom is bonded to another atom.

Hybridization

The way this works is by combining the orbitals to give new orbitals of equal energy. This is called the **hybridization** of atomic orbitals.

Bottom line: we can say that an imaginary mixing process converts a set of atomic orbitals to a new set of **hybrid atomic orbitals** or **hybrid orbitals**.

Hybridization

At this level, we consider the following hybrid orbitals:

a) sp

b) sp^2

c) sp^3

HYBRIDIZATION OF CARBON

The element, carbon, is one of the most versatile elements on the periodic table in terms of the number of compounds it may form.

It may form virtually an infinite number of compounds.

Since both the 2s and the 2p sublevels are half-filled, the excited state is relatively stable.

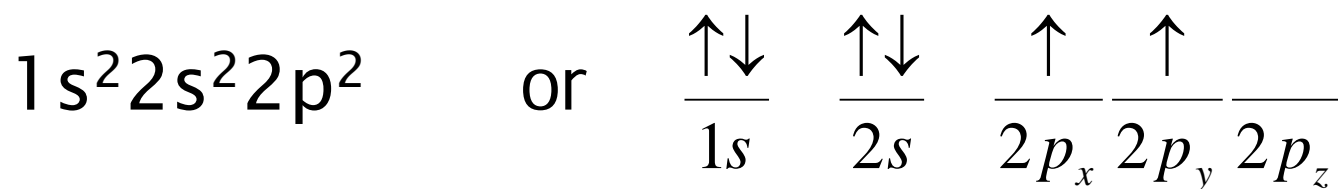
HYBRIDIZATION OF CARBON

This is largely due to the types of bonds it can form and the number of different elements it can join in bonding.

Carbon may form single, double and triple bonds. The hybridization of carbon involved in each of these bonds will be investigated in this handout.

HYBRIDIZATION OF CARBON

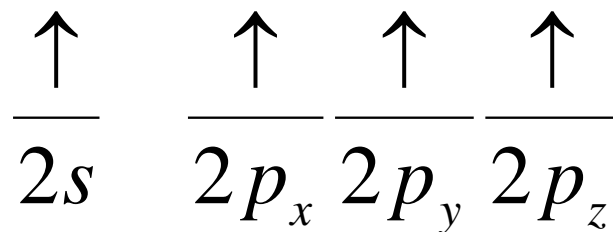
From the ground state electron configuration, one can see that carbon has four valence electrons, two in the 2s subshell and two in the 2p subshell.



HYBRIDIZATION OF CARBON

The 1s electrons are considered to be core electrons and are not available for bonding.

Carbon will form an excited state by promoting one of its 2s electrons into its empty 2p orbital and hybridize from the excited state.



HYBRIDIZATION OF CARBON

By forming this excited state, carbon will be able to form four bonds. The excited state configuration is known as *sp³ hybridized*.

Recall that energy is released when bonds form, so it would be to carbon's benefit to try to maximize the number of bonds it can form.

HYBRIDIZATION OF CARBON

In order to determine the hybridization on a carbon atom, one must first draw the Lewis structure. From the Lewis structure, count the number of groups (things attached) around the central carbon.

A group represents the regions of electron density around the carbon and **may be single, double or triple bonded.**

Let's look at an example of each of the hybridizations of carbon.

For our first example, let's choose methane, CH_4 . Draw the Lewis structure.

Explanation of CH₄

This Lewis structure shows **four groups around the carbon atom**. This means four hybrid orbitals have formed. In order to form four hybrid orbitals, four atomic orbitals have been mixed. The s orbital and all three p orbitals have been mixed, thus **the hybridization is sp^3**

Let's look at an example of each of the hybridizations of carbon.

For our first example, let's choose ethylene, C_2H_4 . Draw the Lewis structure.

Explanation of C₂H₄

This Lewis structure shows **three groups around the carbon atom**. This means three hybrid orbitals have formed. In order to form three hybrid orbitals, three atomic orbitals have been mixed. The s orbital and all two p orbitals have been mixed, thus the **hybridization is sp²**

Let's look at an example of each of the hybridizations of carbon.

For our first example, let's choose acetylene, C_2H_2 . Draw the Lewis structure.

Explanation of C_2H_2

This Lewis structure shows **two groups around the carbon atom**. This means two hybrid orbitals have formed. In order to form this bond, two atomic orbitals have been mixed. The s orbital and one p orbital have been mixed, thus **the hybridization is sp**

Hybridization

The number of groups represents how many hybrid orbitals have formed. The number of hybrid orbitals formed equals the number of atomic orbitals mixed. The description of the atomic orbitals mixed is equivalent to the hybridization of the carbon atom.

Summary of hybrid bonds

Hybridization	Orbitals involved	Sites for bonding
sp^3	1 s & 3 p's	4
sp^2	1 s & 2 p's	3
sp	1 s & 1p	2

Resonance

There are a number of compounds and polyatomic ions that cannot be written using one single Lewis structure.

Linus Pauling developed what today is called "resonance theory."

Resonance

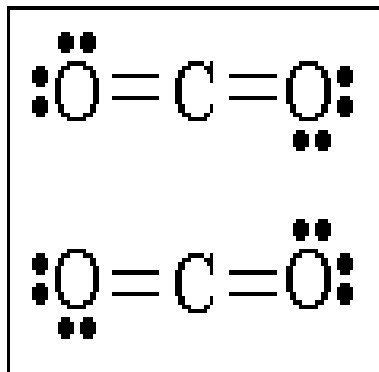
Resonance happens when more than one valid Lewis dot-diagram (or what Pauling calls a valence-bond structure) can be written for a molecule or ion.

When this happens, the true structure is a blend of all the different possible structures.

Resonance

Here is another example, using the molecule CO_2 :

Carbon Dioxide Resonance Structures



Resonance

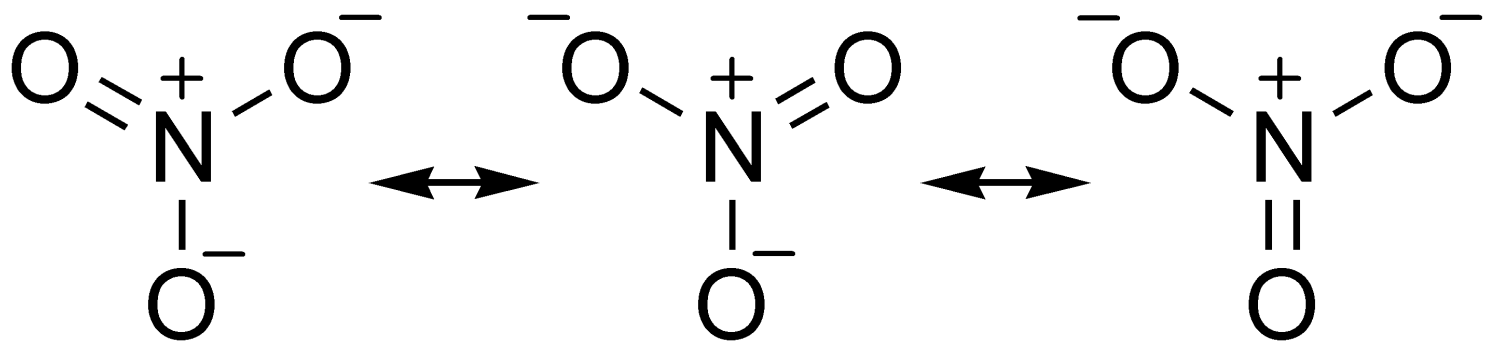
OK, here's the deal. Neither one of those two structures really does exist.

The real molecule that exists in nature is a "resonance hybrid" between the two.

The real molecule acts as if it had one and one-half bonds between each of the two structures.

Resonance

The two structures above are merely descriptive aids and, in fact, never exist.
An example of resonance with NO_3^- :



Molecular Polarity

Molecular polarity results when the **entire molecule** (not just a bond in the molecule) **ends up with an unequal distribution of electron pairs.**

An asymmetrical arrangement typically results in unshared pair or pairs of electrons all in one area of the molecule.

Molecular Polarity

or, when different outer atoms, such as Groups 15, 16, or 17 elements, are attached to one end of a molecule.

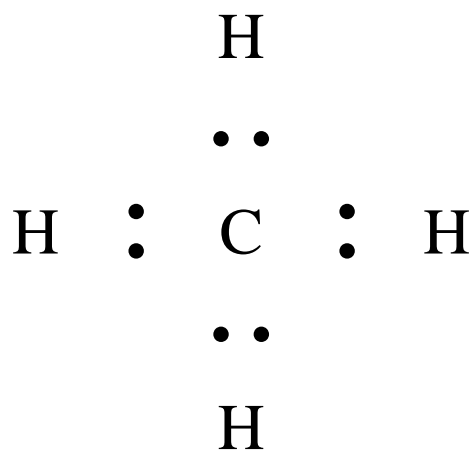
A polar molecule is said to have a **dipole**.

In other words one part of the molecule has a slight positive charge (δ^+) AND one part is slightly negative (δ^-)

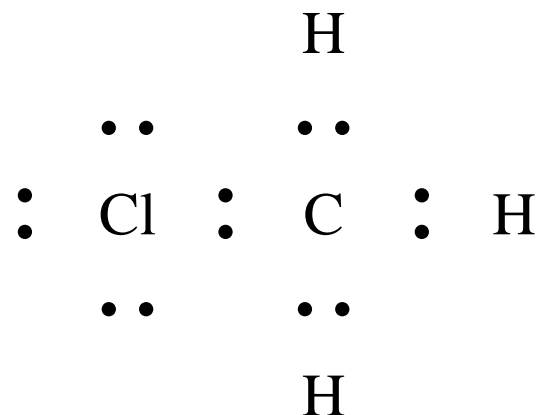
Molecular Polarity

A molecule will be nonpolar when there is an equal distribution of electron pairs all of the outer atoms around the central atom are identical.

Molecular Polarity



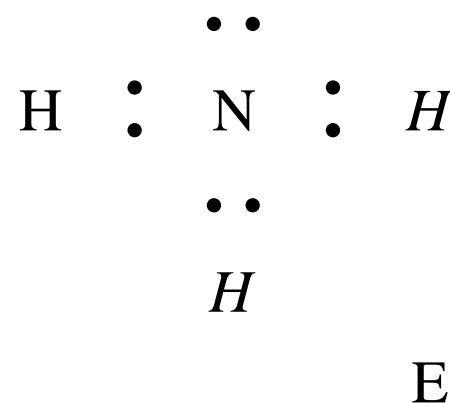
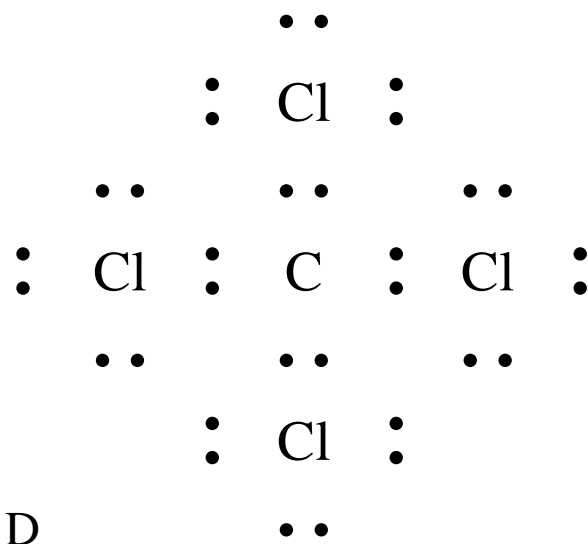
A



B

On the this slide, molecule “A” is nonpolar while molecule “B” is quite polar.

Molecular Polarity



On these examples molecule D is nonpolar while molecule E is polar